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Synchrotron X-Ray Radiolysis of Peptides Reveal Reactivities of Amino Acids

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ABSTRACT: Radiolysis of peptide and protein solutions with high-energy X-ray beams induces stable, covalent modifications of some amino acid residues. In order to elucidate protein structures in solutions, radiolytic modification reactions are being correlated to solvent accessibility of residues. These studies provide a foundation for a new protein footprinting method.

Hydroxyl radicals react preferentially with the side chains of aromatic, heterocyclic or sulfur-containing amino acids. The rates of these side chain modifications by hydroxyl radicals have been directly measured with pulsed radiolysis and photolysis studies to be $5 \times 10^9 - 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

A series of peptides of varied sequences are selected to study their synchrotron radiolysis chemistry. Radiolyzed peptide products are detected within 10 milliseconds of exposure to a white light synchrotron X-ray beam. Mass spectrometry techniques are used to characterize radiolytic modification to amino acids cysteine (Cys), methionine (Met), phenylalanine (Phe), tyrosine (Tyr), tryptophan (Trp), proline (Pro), histidine (His) and leucine (Leu). A reactivity order of Cys, Met \gg Phe, Tyr, $>$ Trp $>$ Pro $>$ His, Leu has been determined under aerobic reaction conditions from MS/MS analysis of the radiolyzed peptide products.